

BORON-DOPED ISOTOPIC DIAMOND AND PROCESS FOR PRODUCING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to a ^{12}C isotopic diamond or a ^{13}C isotopic diamond which is boron-doped and has a high thermal conductivity, and a process for producing the same. In the present specification, a
10 diamond purified to ^{12}C (namely, in the isotopic ratio, the amount of ^{12}C in the purified diamond is increased to more than that of a natural diamond) is referred to as a ^{12}C diamond or a ^{12}C isotopic diamond properly.

2. Prior Art

15 Since diamond has the highest hardness (Mohs hardness: 10) in known substances and an outstanding abrasion resistance, it is employed for tools such as a whetstone, an abrasive material, a die, a boring bit, a cutting tool, a coating tool and the like. In addition,
20 since it has a high velocity of sound, it is utilized for a high-sound-generating speaker diaphragm.

Moreover, diamond has the highest thermal conductivity in all substances at room temperature, and this characteristic is exhibited more at a higher purity.
25 Hence, it is combined into electronic parts as a heat sink material. However, since diamond is an electrically insulating material itself, it has been limited to a simple application such as said heat sink material.

A carbon or a carbon compound present in nature
30 contains about 1.1% of ^{13}C in addition to ^{12}C , and this is also true of a natural diamond. It is known that a diamond with a purified carbon isotope has an improved thermal conductivity as compared with a diamond with a natural ratio. For example, in "Physical Review B",

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Vol. 42, No. 2, pp. 1104-1111 (July 15, 1990), it is reported that a diamond with ^{12}C of 99.93% is synthesized employing 99.9% $^{12}\text{CH}_4$, and that said diamond has a thermal conductivity about 1.5 times as high as that of a diamond with a natural isotopic composition.

According to the report, a ^{12}C diamond single crystal is synthesized as a sample thereof by preparing a diamond sheet according to the CVD method employing a 99.9%-enriched $^{12}\text{CH}_4$, pulverizing the sheet into a powder, and growing the crystal on a small diamond seed crystal from a molten transition metal at a pressure of 52000 atm. and a temperature of 1200°C. According to the above method of synthesis, it is necessary, first of all, to prepare a diamond powder as a carbon source according to the CVD method. However, the yield according to the CVD method is generally of the order of 1%, hence, even if the above material is employed, a process of obtaining a powder thereof is also needed in order to synthesize a diamond single crystal, and besides, there exists a large problem regarding the yield thereof.

The thermal conductivity of diamond is very liable to be influenced by crystal quality, and also in the case of a ^{12}C isotopic diamond, if the crystal quality is poor, it is difficult to generate a high thermal conductivity according to ^{12}C purity. In addition, it is known that if diamond contains impurities, such as nitrogen or impurities being added thereto, the thermal conductivity decreases. Japanese Patent Publication No. 4-92894 reports that a synthesized diamond with a high thermal conductivity is obtained by applying a gas phase synthesis technique, employing ^{12}C or ^{13}C wherein more than 99.9% of the carbon is carbon isotopes, and adjusting the incorporation of nitrogen to less than 20 ppm.

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In addition, it is known that diamond is doped with boron to be a p-type semiconductor and a boron-doped diamond is expected to be employed as a semiconductor device and a luminescent device. However, boron doped to the diamond becomes an impurity to the diamond. Because of this, it has been thought to be difficult for a ^{12}C isotopic diamond sensitive to crystal quality to express a high thermal conductivity, and this is also true of a boron-doped diamond and, needless to say, a boron-doped ^{12}C isotopic or ^{13}C isotopic diamond.

That is, it has been thought that a dopant, boron, scatters phonons, a main factor in the conduction of heat in a diamond, and that, in a boron-doped and isotopically purified diamond, the improvement in thermal conductivity is small. For this point, for example, when a boron-doped diamond is applied to a semiconductor device or an optical material as an example of application, it may cause heat concentration and it has been thought that, in such a case, the effect of a high thermal conductivity according to isotopic purity cannot be utilized because of the above point.

SUMMARY OF THE INVENTION

When the present inventors actually synthesized a boron-doped and isotopically purified ^{12}C isotopic diamond and measured the thermal conductivity thereof, they unexpectedly found that it retained the electrical conductivity of a p-type semiconductor according to the addition of boron and a high thermal conductivity according to ^{12}C purity. That is, the present invention provides a ^{12}C or ^{13}C isotopic diamond which is boron-doped, is isotopically purified and has a high thermal conductivity of about 15-50%, preferably 30-50%, higher than that of a high-purity diamond having a natural

isotopic ratio at room temperature and a process for producing the same.

5 The present invention provides a ^{12}C or ^{13}C isotopic diamond which is boron-doped, has a high thermal conductivity and is isotopically purified, and it also provides a luminescent device comprising a ^{12}C or ^{13}C isotopic diamond which is boron-doped, has a high thermal conductivity and is isotopically purified. Moreover, the present invention provides a semiconductor device
10 comprising a ^{12}C or ^{13}C isotopic diamond which is boron-doped, has a high thermal conductivity and is isotopically purified.

15 In addition, the present invention provides a process for producing a ^{12}C or ^{13}C isotopic diamond single crystal, wherein a diamond single crystal is formed on a seed crystal diamond by using a carbon comprising isotopically purified ^{12}C or ^{13}C as a material, employing a flux containing a nitrogen getter, adding boron into said material or the flux, or around said material and the
20 flux, and diffusing said carbon material into the flux under a high pressure and a high temperature. Moreover, the present invention provides a process for producing a ^{12}C or ^{13}C isotopic diamond which is boron-doped and has a high thermal conductivity, wherein a diamond is formed in
25 a thin-film state on a substrate placed in a reaction atmosphere by employing a mixed gas of an isotopically purified hydrocarbon or carbon monoxide or carbon dioxide by ^{12}C or ^{13}C or at least two thereof, and hydrogen as a material, and adding a doping component thereto.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a view showing one example of a sample constitution according to the temperature gradient method.

Fig. 2 is a view of the sample constitution employed in the present examples.

Fig. 3 is a view showing the ultrahigh-pressure device employed in the present examples.

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PREFERRED EMBODIMENTS OF THE INVENTION

A ^{12}C isotope or a ^{13}C isotope in a diamond according to the present invention needs to have a purity (degree of isotopic purification) of at least 99.5%, preferably at least 99.9%, more preferably at least 99.94%. In the present invention, a p-type semiconductor can be obtained by doping boron to an isotopically purified ^{12}C isotopic diamond or ^{13}C isotopic diamond, and said p-type semiconductor has a high thermal conductivity of from about 26-31 W/cm $^{\circ}\text{K}$ or about 15-50%, preferably 30-50%, higher than that of a high-purity diamond having a natural isotopic ratio at room temperature.

Here, the amount of boron doped is not particularly restricted so long as it is in an amount allowing a function as a p-type semiconductor to be exhibited. Preferably it is less than 100 ppm, more preferably less than 60 ppm, and according to the amount of boron added where the thermal conductivity (half-band width of a Raman spectrum) begins to decrease, it is preferably of the order of 30-40 ppm to about 3-4 ppm, or less.

As described above, boron doped to diamond becomes an impurity to the diamond, and hence, it has been thought to be hard for a ^{12}C diamond sensitive to crystal quality to express a high thermal conductivity.

In the present invention, completely inversely to such a perception or technical common knowledge, a p-type semiconductor can be obtained by doping boron to an isotopic diamond comprising isotopically purified ^{12}C or an isotopic diamond comprising isotopically purified ^{13}C ,

molten metal (including alloys) such as Fe, Co and Ni. Examples of the flux method include a film growth method and a temperature gradient method. The film growth method is a method utilizing the fact that graphite and diamond have a different solubility in molten metals, wherein when a molten metal and graphite come into contact with each other at a high pressure, the graphite is dissolved and diffused, and just after then (at the rear of the molten metal film) a diamond is precipitated.

On the other hand, the temperature gradient method is a method utilizing the fact that diamond has a different solubility in molten metals according to a temperature (temperature difference: about from 20 to 50°C), wherein, to the molten metal phase heated at a high pressure, one is retained at a high temperature to dissolve a carbon material, while the other is retained at a lower temperature to precipitate a diamond. In the temperature gradient method, large grains of diamond are grown on a diamond seed crystal placed at a low temperature region, wherein the formation of spontaneous nuclei occurring is suppressed and the dissolution of the seed crystal is suppressed till the occurrence of diamond growth by arranging a diamond nucleation suppressing layer and an isolation layer at the upper part of the seed crystal.

Fig. 1 shows an example of "the sample constitution" and the like introduced heretofore for the above temperature gradient method ("Technology for Treating Resources", Vol. 37, No. 1 (90, spring), pp. 23-28). In Fig. 1, 1 indicates a carbon source, 2 is a metal solvent, 3 is platinum foil, and 4 is a diamond seed crystal. The constitutional sample is put into a capsule of an NaCl molded article, and the capsule is packed in a cylindrical heater so that the carbon source should be at

the center of the heater. In the cylindrical heater, the central part has a high temperature and both ends have a low temperature, and hence the metal solvent can have a temperature gradient according to this temperature distribution.

Subsequently, the capsule is packed in a high-pressure vessel, pressed to about 60,000 atm., heated to about 1400°C for from 15 to 24 hours, and thereby a crystal of from 2 to 3 mm as shown with the mark 5 in Fig. 1 is obtained. It is described that, in this case, the above platinum foil 3 is for protecting the seed crystal lest the seed crystal dissolve in the metal solvent to disappear at the time of the start of crystal growth. According to the above document, the platinum foil 3 dissolves in the metal solvent to disappear gradually with time, but the metal solvent is saturated with carbon at this time, and hence the diamond seed crystal 4 does not dissolve.

In the case of synthesizing a diamond single crystal by the temperature gradient method, a diamond, graphite or a mixture thereof is employed as a carbon source. In the present invention, also in the case of producing a ^{12}C or ^{13}C isotopic diamond single crystal by the temperature gradient method, these carbons may be employed as a carbon source. However, a pyrolytic carbon, a diamond synthesized by chemical deposition or a diamond-like carbon synthesized by chemical deposition is preferably employed.

For example, Japanese Patent Publication No. 4-108532 suggests a technique of producing a single crystal diamond with a high isotopic purity and a high thermal conductivity by the same temperature gradient method by preferably employing a diamond obtained by the CVD (chemical vapor deposition) method as a carbon

sheet, and then releasing it from the substrate. In Table 1, the BAF value is obtained by employing an X-ray diffraction technique, and the larger the numerical value, the larger the anisotropy. The BAF value of ordinary graphite is less than 2.

Table 1

Kind of pyrolytic carbon	Structure by optical microscope	Density (bulk density) (g/cm ³)	BET surface area (m ² /g)	BAF value	Lattice constant of C axis (Å)
Flake-like	Columnar	1.10	3.1	3~20	6.8~7.0
Soot-like	Non-columnar	0.87	55.6	about 1	6.8~7.0

In the present invention, in the case of employing a flake-like pyrolytic carbon as a carbon source, a diamond containing ¹²C or ¹³C at a high ratio can be produced by selecting the ratio of a carbon isotope in a hydrocarbon gas material or a carbon monoxide material, for example, the ratio of ¹²C or ¹³C in methane, at the time of producing a flake-like pyrolytic carbon, namely, by employing methane with a varied isotopic composition.

The pressure and temperature to be applied in the performance of the present invention is not particularly restricted so long as they are within the conditions of a diamond stable region, preferably, it can be performed at a pressure of from about 5 to 6.5 GPa and at a temperature of from about 1300 to 1500°C. As a flux, any metal or alloy (including mixtures) known as those used in the flux method can be employed. Preferably Fe, Co, Ni and alloys of these metals can be employed, and a component as a boron source, for example, boron, is added thereto. Moreover, a diamond not containing nitrogen as an impurity or substantially not containing nitrogen can

be obtained by employing a flux containing a nitrogen getter (Ti, Zr, Al and the like) on demand.

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EXAMPLES

Hereafter, the present invention will be described in more detail according to examples. It goes without saying that the present invention is not restricted to these examples. Examples according to the temperature
10 gradient method will be described but the same can be applied to the gas phase method. Fig. 2 and Fig. 3 show the sample constitution and the ultrahigh-pressure device employed in the present examples respectively.

As shown in Fig. 2, the sample constitution is
15 almost similar to the sample constitution shown in Fig. 1, and the same marks are used about common parts in Fig. 1 and Fig. 2. 1 shows a carbon source, 2 is a metal solvent (= flux), 3 is a platinum foil, and 4 is a diamond seed crystal. The platinum foil 3 is placed
20 between the diamond seed crystal 4 and the flux 2, and prevents the seed crystal 4 from dissolving at the initial stage of the production operation. In addition, 6 shows a graphite heater, 7 is a pressure medium, and 8 is an iron sealing ring for sealing the pressure medium 7
25 provided therearound. In the present examples, a metal solvent containing a nitrogen getter was employed as the flux 2, and "NaCl + 10 wt.% ZrO₂" as the pressure medium 7 for transmitting the pressure uniformly.

When the sample constitution (sample constituted as
30 above) is retained under the condition where the diamond is stable and under the conditions of a high temperature and a high pressure for the flux to dissolve, a diamond single crystal grows on a seed crystal. In the case of employing a cylindrical heater, the central part thereof

has a relatively high temperature and the upper and lower circumference thereof has a low temperature, hence, utilizing this feature, a temperature difference can be made between the central side (high temperature) and the lower side (low temperature) of the flux. For this, the carbon source is placed so that it should be located at the central part, namely, the high-temperature part, and thereby the carbon material at the upper side at a high temperature is dissolved in the flux and precipitated as a diamond single crystal on the seed crystal at the lower side at a low temperature.

Fig. 3 shows the cross-section of a so-called flat-belt-type ultrahigh-pressure device employed in the present examples. As shown in the drawing, the device essentially comprises cylinders and anvils of an ultrahard alloy, and 9 in Fig. 3 shows a gasket. The gasket 9 is for sealing between the anvils and the cylinders, and in the present examples, pyrophyllite is employed as a material for it.

The sample composition is placed between the space formed by the cylinders and the anvils as shown in Fig. 2, and heating is performed by running an electric current from the anvil to the graphite heater 6 through a stainless steel electrode 11, an electroconducting ring (iron) 12 and a molybdenum electrode 10. On the top and the bottom of the graphite heater 6 are provided zirconia plates 13 for insulation.

Examples

A diamond single crystal according to the present invention was produced by employing the sample constitution of Fig. 2 and the ultrahigh-pressure device of Fig. 3. As a carbon source was employed a product obtained by thermally decomposing an isotopically

purified ^{12}C methane gas ($^{12}\text{CH}_4$, purity: more than 99.95%) obtained from LNG by rectification without employing a carrier gas (namely, 100% methane) at a decomposition treatment temperature of 1900°C and at a pressure in the furnace of 2 Torr, depositing it on a graphite substrate and releasing it therefrom. It has a columnar structure according to an optical microscope, a bulk density of 1.10 g/cm^3 , a BAF value of 5 and a BET surface area of $3.1\text{ m}^2/\text{g}$.

10 Boron was added (amount of addition: 1000 ppm) to 231 mg of this flake-like pyrolytic carbon, and the mixture was employed as the carbon source 1. The above carbon source 1 was placed on the flux 2 of a metal solvent containing a nitrogen getter to form a sample composition as shown in Fig. 2, and this sample composition was placed in the cylinders in Fig. 3.

15 Thereafter, the pressure medium 7 was pressed to 6.3 GPa by upper and lower anvils. After pressing, an electric current (AC, 2.69 V, 664 A (ampere)) was run to the graphite heater 6 through the stainless steel electrode 11, the electroconducting ring 12 and the molybdenum electrode 10 to heat it to 1450°C . In this case, the operation temperature was calibrated by a Pt/Pt 13% Rh thermocouple.

25 After the above operation state was maintained for 110 hours, the electric current was cut and then the pressing state was released to obtain a diamond single crystal. The produced diamond had a weight of 76.4 mg, and the facets on the surface of the crystal were mainly {100} and {111}. In the same manner as above, diamond single crystals were produced by employing products obtained by adding boron of 1000 ppm, 3000 ppm, 1%, 3% and 10% (mol) respectively to a flake-like pyrolytic carbon obtained from a ^{12}C methane gas as a carbon source.

Comparative Examples

In the same manner as the above technique, a non-boron-doped (namely, produced without adding boron to a carbon source) diamond with a natural isotopic ratio ($^{12}\text{C} = 98.9\%$), a boron-doped (namely, produced by adding boron to a carbon source) diamond with a natural isotopic ratio ($^{12}\text{C} = 98.9\%$), and a non-boron-doped ^{12}C diamond ($^{12}\text{C} = 99.95\%$ or more) were produced. The amount of boron and the thermal conductivity of each of the thus obtained diamonds were measured. The thermal conductivity here was measured by the following measurement 1.

Measurement of the Amount of Boron

Employing a microscopic Fourier transform infrared spectrometer (Janssen Micro FTIR Spectrometer, manufactured by JASCO corporation) as a device, the quantitative determination of boron was conducted according to the strength of the absorption peaks of 1280 cm^{-1} and 2800 cm^{-1} by boron in the diamonds. The amount of boron contributing to the electrical conductivity in the diamonds (effective acceptor density) is determined by this method. In Table 2, the concentration of boron shows the above measured values. Table 2 also shows the amounts of boron added to the carbon material source (amounts of boron incorporated into the material).

Measurement of Thermal Conductivity 1

The FWHM (full width at half maximum) of a Raman peak indirectly has a correlation with thermal conductivity, and it is thought that, in a diamond with a high crystal quality, the smaller the FWHM of a Raman peak is, the higher the suggested thermal conductivity. The measurement of a Raman spectrum was conducted by a

No.	Kind of Diamond	Amount of Boron in Carbon Source	Concentration of Boron	FWHM (full width at half maximum) of Raman peak
Example 1	^{12}C diamond ($^{12}\text{C} = 99.95\%$ or more)	1000 ppm	3~4 ppm	1.54 cm^{-1}
Example 2	^{12}C diamond ($^{12}\text{C} = 99.95\%$ or more)	3000 ppm	9~19 ppm	1.54 cm^{-1}
Example 3	^{12}C diamond ($^{12}\text{C} = 99.95\%$ or more)	1%	29~38 ppm	$1.55\sim 1.59 \text{ cm}^{-1}$
Example 4	^{12}C diamond ($^{12}\text{C} = 99.95\%$ or more)	3%	90~105 ppm	$1.57\sim 1.70 \text{ cm}^{-1}$
Example 5	^{12}C diamond ($^{12}\text{C} = 99.95\%$ or more)	10%	===	1.8 cm^{-1}

Note ---: Nil
 ===: Unmeasured

- 5 As shown in Table 2, the FWHM of the Raman spectrum of the comparative example, namely, the ^{12}C diamond ($^{12}\text{C} = 99.95\%$ or more), is 1.54 cm^{-1} , which corresponds to a thermal conductivity of about 31 W/cm K. In contrast, all of the ^{12}C diamond ($^{12}\text{C} = 99.95\%$ or more) of Example 1, 10 the ^{12}C diamond ($^{12}\text{C} = 99.95\%$ or more) of Example 2 and the ^{12}C diamond ($^{12}\text{C} = 99.95\%$ or more) of Example 3 show the equal FWHM of a Raman peak as the above ^{12}C diamond of Comparative Example 4 and have a high thermal conductivity. Boron is an impurity to diamond and 15 decreases the thermal conductivity according to conventional technical common knowledge, however, the present invention shows that doping of boron has no influence upon thermal conductivity.

Measurement of Thermal Conductivity 2

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The measurement according to the FWHM of a Raman peak in the above measurement 2 is an indirect method, but the present measurement 2 is a direct method. As a device was employed a steady-state high thermal conductivity measurement device (TS/LA-8550, manufactured by Rigaku). As a sample was employed diamonds of $2 \times 0.3 \times 3$ mm obtained in the above process of production. Both ends of a diamond sample were held by a golden probe ($2 \times 2 \times 8$ mm), and a temperature difference was provided on both ends of the probe. It was retained under a vacuum till it reached a steady state, and temperature gradients of the sample and the probes coated with a graphite paste in advance were measured by an infrared detector.

The thermal conductivity (λ_{Sample}) of the sample was calculated by the formula below according to the temperature gradient of the sample and that of the golden probe. In the formula (1), λ_{Au} denotes the thermal conductivity of the golden probe, $(dT/dL)_{\text{Au}}$ and $(dT/dL)_{\text{Sample}}$ denote the temperature gradient of the golden probe and that of the sample respectively, and A_{Au} and A_{Sample} denote the sectional area of the golden probe and that of the sample respectively. Table 3 shows typical examples of the thus obtained results.

The present measurement of thermal conductivity is conducted when the temperature of the sample is about 36°C , and since the scattering of phonons which interfere with the conduction of heat is smaller at a lower temperature, the measured value of thermal conductivity at room temperature is guessed to be higher.

Formula 1

Table 3

No.	Kind of diamond	^{12}C isotopic ratio	Doping	Thermal conductivity (W/cm K)	Electrical characteristic
1	Diamond with natural isotopic ratio	98.9%	Nil	22.3	Insulator
2	"	"	"	22.9	"
3	"	"	"	22.6	"
4	^{12}C diamond	$\geq 99.95\%$	Nil	31.8	Insulator
5	"	"	"	31.8	"
6	"	"	"	29.9	"
7	Diamond with natural isotopic ratio containing boron	98.9%	Boron = 3~4 ppm	23.9	p-type semiconductor
8	^{12}C diamond containing boron	$\geq 99.95\%$	Boron = 3~4 ppm	30.6	p-type semiconductor
9	"	"	Boron = 30~40 ppm	28.0	"

As is apparent from Table 3, the diamond with a natural isotopic ratio containing no boron is an insulator for its electrical characteristic, and exhibits a thermal-conductive characteristic of a thermal conductivity of about 23 W/cm K. The diamond with a natural isotopic ratio containing boron is a p-type semiconductor for its electrical characteristic, and the thermal conductivity thereof is about 24 W/cm K. In contrast, the ^{12}C purified diamond (^{12}C isotope $\geq 99.95\%$) containing boron of from 3 to 4 ppm is a p-type semiconductor and exhibits a thermal-conductive characteristic of a thermal conductivity of about 31 W/cm K, and the same ^{12}C purified diamond, which contains boron of from 30 to 40 ppm, exhibits an excellent value of a thermal conductivity of about 28 W/cm K. The reason

why the amount of boron doped ranges from 30 to 40 ppm is that boron was distributed in the sample within this range.

5 Example 6

An RF plasma CVD device (RPS-0404 made of Nippon RF Co. Ltd.) was used as a device for producing a film. Film synthesis conditions were as described in Table 4. Methane ($^{12}\text{CH}_4$) of ^{12}C isotopic purification of 99.95% was used as CH_4 for synthesis, and 1000 ppm (=B/C) of $\text{B}(\text{CH}_3)_3$ was added for doping boron, thereby producing a diamond film.

An RF plasma CVD film obtained by the above device was analyzed, and the result revealed the quality of a diamond excellent in Raman spectrum analysis and cathode luminescence analysis.

Table 4

Film Synthetic Parameter	Film Synthetic Condition
Power of RF	45kW
Pressure	26.7kPa(200Torr)
Gas and Flow Rate	Ar: 31.8 l/min H ₂ : 11.2 l/min CH ₄ : 0.17 l/min B(CH ₃) ₃ : 1000ppm (=B/C)
Concentration of Methane	0.4 vol% of Flow Rate of Entire Raw Material Gas
Film Synthetic Time	30 hours
Substrate Temperature	900°C
Substrate Holder	Suction Type Holder Made of Copper
Substrate	Mo Plate: 50mmø (thickness = 5mm)

20 Comparative Example 5

In the same manner as Example 1, using methane with a natural isotopic ratio containing methane as CH_4 for synthesis among a film synthesis condition in the Table 4, adding 1000 ppm (=B/C) of $\text{B}(\text{CH}_3)_3$, thereby producing a diamond film.

Comparative Example 6

In the same manner as the Comparative Example 5 except for the non-addition of $B(CH_3)_3$, methane ($^{12}CH_4$) of ^{12}C isotopic purification of 99.95% has used as CH_4 for synthesis, thereby producing a diamond film.

Comparative Example 7

In the same manner as the Comparative Example 5 except for the non-addition of $B(CH_3)_3$, natural isotopic methane with a natural isotopic ratio containing methane was used as CH_4 for synthesis, thereby producing a diamond film.

Measurement of the Amount of Boron:

The measurement was conducted using the same measuring device as the device for measuring amounts of boron of a high-pressure synthetic diamond of the first example.

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Measurement of Thermal Conductivity:

The measurement was conducted using the measuring device as the device for measuring thermal conductivity of a high-pressure synthetic diamond of the first example.

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As a method of processing a sample, the diamond film obtained by a pre-processing process was cut to a size of 2 mm × 3 mm (width × length), also of 2 mm × 4 mm and they are respectively polished by the depth of 20 μm from the back side of the film, thereby respectively producing two samples serving as samples for measuring thermal conductivity.

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Result of Measurement of Thermal Conductivity of the CVD Diamond

Table 5 shows a result of measurement of a thermal conductivity of samples produced by the CVD method.

- 5 As evident from Table 5, the diamond with a natural isotopic ratio represents an insulator for its electrical characteristic, and also represents a thermal conductivity of 21 W/cm·K. The diamond with a natural isotopic ratio containing boron is a p-type semiconductor
- 10 for its electrical characteristics, and the thermal conductivity thereof is about 20 W/cm·K. On the other hand, the ^{12}C purified diamond containing boron of 20 ppm is a p-type semiconductor for its electrical
- 15 conductivity of 26 W/cm·K.

Table 5

No.	Kind of Diamond	^{12}C isotopic ratio	Presence of Doping	Thermal conductivity (W/cm·K)	Electrical Characteristic
Comp. Ex. 7	Diamond with Natural Isotopic ratio	98.9%	None	20.5	Insulator
Comp. Ex. 6	^{12}C Diamond	$\geq 99.95\%$	None	27.5	Insulator
Comp. Ex. 5	Diamond with Natural Isotopic Ratio Containing Boron	98.9%	Boron = 20 ppm	19.5	P-type Semiconductor
Example 6	^{12}C Diamond Containing Boron	$\geq 99.95\%$	Boron = 20 ppm	26.2	P-type Semiconductor

According to the present invention, a ^{12}C or ^{13}C isotopic diamond which is boron-doped and has an extremely high thermal conductivity can be obtained. Said ^{12}C isotopic diamond or ^{13}C isotopic diamond which is
5 boron-doped and has a high thermal conductivity is an excellent material in a utility related to heat, such as a semiconductor device and a luminescent device.

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